

In Situ Chemical Stabilization of Metals and Radionuclides
Through Enhanced Anaerobic Reductive Precipitation:
Application of a Commercial Technology to DOE Needs

David S. Liles (dliles@arcadis-us.com, 919-544-4535)
Christopher C. Lutes (clutes@arcadis-us.com, 919-544-4535)
Gregory B. Page (gpage@arcadis-us.com, 865-481-3000)
Dr. Suthan S. Suthersan (ssuthersan@arcadis-us.com, 215-702-3250)
ARCADIS G&M
4915 Prospectus Drive, Suite F
Durham, NC 27713

Abstract

Geochemical theory and ARCADIS G&M's (ARCADIS) field experience show that many metals and radioactive isotopes of these metals that are dissolved in groundwater can be reduced to less harmful forms and/or irreversibly precipitated to prevent migration through the implementation of the *In Situ* Reactive Zone (IRZ) technology. In many cases, the IRZ technology returns the metallic contaminants to the naturally occurring, stable mineral form in which they were originally mined. This poster describes ARCADIS' successful commercial and Department of Defense (DoD) experience in remediating a variety of metals (including Cr⁺⁶, Cd, Pb, Ni, Zn, and U), and chlorinated solvents (including TCE, DCE, VC, CT, and CF) at more than eighty sites using the IRZ remedial technology. The IRZ technology stimulates indigenous microbiological organisms through the engineered addition of low cost food grade electron donors to precipitate metals as hydroxides or sulfides and degrade chlorinated organics. ARCADIS will demonstrate with DOE NETL funding at the bench- and field- scale that the IRZ technology can cause the irreversible *in situ* precipitation of uranium and/or technetium and simultaneously treat other compounds of concern to DOE.

ARCADIS has successfully applied the IRZ technology:

At Various Constituent Concentrations – We have successfully treated chromium concentrations in groundwater at levels greater than 100 mg/L. For chlorinated VOCs we have had success in treating areas containing dissolved concentrations in excess of 50 mg/L. We have also treated much more dilute plumes with concentrations of target constituents in the 10 – 100 µg/L range.

In Varied Geologies – To date, ARCADIS has applied the IRZ technology at sites with widely differing geologic and hydrogeologic settings, from low permeability silts and clays, to high permeability alluvial deposits, to bedrock settings and with groundwater velocities ranging from a few feet per year to several feet per day.

Under Multiple Regulatory Programs – The IRZ technology has been applied under multiple regulatory programs, including CERCLA and RCRA, and under the jurisdiction of politically sensitive regulatory agencies such as the California Regional Water Quality Control Board.

The creation and maintenance of the IRZ, at most sites, requires limited numbers of reagent injection events. These injection events are typically performed in a batch mode and require only one to two days per event. At most sites, injection events are required only once or twice per month in the early stages of the project (first three to six months when IRZ is developed) and injection events are normally scaled back to monthly or even quarterly timing during later stages of a project. Projects typically require one to three years to complete in the field at full-scale implementation. Therefore the resources required are limited compared to many other techniques, and the complete *in situ* nature of the IRZ technology, as well as the infrequent injection events, results in a minimal impact to other site activities.

The use of these low-cost food grade reagents provides many benefits, including:

- The material is competitively available from many commercial suppliers and is very economical.
- Typically no regulatory, public, or stakeholder concern exists regarding reagent handling at a site or the introduction of a food grade reagent into the environment.
- Since indigenous bacterial communities support this remedial technology, IRZ requires none of the special permitting and involves no concerns about survival, both of which accompany bio-augmentation projects.

While an in-depth knowledge of the technology and the site biogeochemistry is required to properly engineer these systems, the technology is simple to apply in the field. Personnel needed for the reagent injection and IRZ maintenance require little or no specialized skills or training. In ARCADIS' numerous commercial applications, we routinely rely on plant and/or site personnel to perform the reagent injections. This provides significant cost savings and enhances teaming between ARCADIS and the stakeholder.

The molasses induced IRZ concept has been developed since 1994, patented in the private sector by ARCADIS, and applied in 20 states and in two foreign countries. This demonstration project furthers a key objective outlined in Approaches to Improve Innovative Technology Development at the U.S. Department of Energy, November 2000, by championing a technology from the commercial sector to meet DOE's specific environmental restoration needs.

Objective

With the close of the Cold War, the U.S. Department of Energy (DOE) turned its attention and resources to cleaning up the legacy of environmental contamination associated with creating and maintaining nuclear defense systems. Sites throughout the country were affected by intentional and unintentional activities and cleanup costs may

be as high as \$350 billion. Reducing the cost of what has been called “the largest single cleanup program in the world” has been a priority of DOE since establishment of the DOE’s Environmental Management program in 1990. DOE has focused considerable effort on the development and efficient deployment of technologies to improve the safety and effectiveness of cleanup and decrease program life cycle cost. Leveraging technologies developed in the private sector to DOE sites can facilitate timely achievement of DOE goals. A recent report by an association of Western states¹ recommended that DoE “champion all technologies including those from the commercial sector.”

The mix of organic/heavy metal contaminants stabilized *in situ* at many of our commercial sites treated to date is similar to groundwater contamination encountered at DOE. The molasses IRZ has a clearly demonstrated track record treating contaminants likely to be encountered at DOE sites including chlorinated organic solvents as well as Cr, U and other metals.²⁻¹⁶ More than 10,000 contaminated sites have been catalogued at 137 current or former facilities operated by DOE. Contamination, as reported in EPA’s *Cleaning up the Nations Waste Sites: Markets and Technology Trends*,¹⁷ included:

- Uranium – 30% of the sites
- Plutonium – 11 % of the sites
- Mercury – 6 % of sites
- Chromium – 5 % of sites
- PCE – 15 % of sites
- Solvents 10 % of sites

Thus, contamination addressable by the proposed IRZ technique is widespread in the DOE complex.

Approach

ARCADIS is a pioneer in *in situ* bio-remediation and holds patents^{18,19} on processes for the creation of reducing conditions in the groundwater in the area(s) of concern, *in situ* reactive zones (IRZ). The creation of reducing conditions through IRZ provides the biogeochemical environment necessary for dissolved metals in the groundwater to form insoluble compounds that precipitate and are immobilized in the soil matrix. These enhanced anaerobic reductive precipitation (EARP) mechanisms are primarily biologically driven, co-metabolic processes. In other words, the indigenous microbes use organic carbon as a primary substrate for obtaining energy and produce hydrogen. The organic carbon (typically, food grade molasses or whey) serves as an electron donor and is oxidized during this process while cationic metals serve as electron acceptors and are subsequently reduced and precipitated as the hydroxide, carbonate or sulfide. Oxygen, nitrate, iron, manganese, sulfate, and carbon dioxide, also serve as electron acceptors and are consumed sequentially in these reactions, making the aquifer progressively more anaerobic and reducing, although the process does not need to proceed all the way to methanogenic conditions to be effective for metals precipitation. An additional treatment

pathway under EARP involves sulfate-reducing bacteria (SRB) that produce hydrogen sulfide that reacts with the contaminant of concern (COC) to form an insoluble sulfide. The technology was first implemented by ARCADIS in 1994 and has since been demonstrated in the bench, pilot, and full-scale forms at numerous sites.

IRZ technology can also be applied to induce or enhance the degradation of CAHs *in situ*. Often, natural processes are limited in rate or stalled at a site due to one or more of the following conditions:

- Aerobic or oxidizing conditions
- Weak reducing conditions
- Deficiency of organic carbon
- Deficiency of electron acceptors
- Deficiency of nutrients
- Stressed bacterial population

Typically, the most common rate-limiting factors that result in slow degradation of CAHs is a lack of organic carbon in the site, that can result in ORP conditions not conducive to reductive dechlorination. Optimal degradation rates can be achieved when carbon concentrations (as measured by total organic carbon/total dissolved organic carbon (TOC/DOC)) are at least 100 times the organic CAH concentrations. Degradation is often slowed due to the depletion of natural organic carbon in the groundwater and the less than optimal reducing conditions present in the aquifer. Once conditions are made optimal, degradation of CAHs usually proceeds rapidly and completely through either co-metabolic or dehalorespiration processes. We have discussed the mechanism of this approach in more detail elsewhere.^{10,11}

The compounds this technology has been successfully applied for include both organics such as:

TCE, DCE, VC, CT, CF, Chlorinated Propanes, PCP, Pesticides

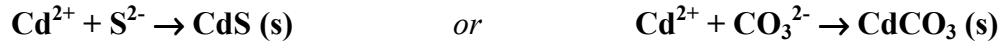
and metals and radionuclides such as:

Cr⁺⁶, Ni, Pb, Cd, Zinc, Hg, U.

The mechanism of this process for metals precipitation is well understood. Following creation of the necessary reducing conditions in the groundwater, two reactions generally occur which will reduce the mobility of the metals. First, any dissolved metals present in higher oxidation states (for example, hexavalent chromium [Cr⁺⁶]) will be reduced (in the case of chromium to trivalent chromium [Cr⁺³]). Second, the dissolved metals (in the more reduced forms) will react with reduced anions present in groundwater such as oxides, carbonates, and sulfides.

Cadmium Mechanism

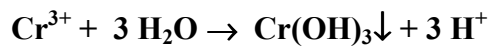
Dissolved cadmium when present in groundwater is thought to react with either sulfide or carbonate present in the aquifer to form the stable cadmium carbonate or cadmium sulfide precipitates as follows:



As discussed above, excess sulfide will be present in the groundwater as a result of the microbial reduction of sulfate occurring naturally in the groundwater at contaminated sites or as a component of the injected molasses solution. Carbonate is naturally present in groundwater and will also be formed as a result of the formation of carbon dioxide from the microbial degradation of the carbohydrates in the molasses solution.

Chromium Mechanism

A second example is chromium. Once the chromium has been reduced, as discussed above it can be rapidly precipitated under alkaline to moderately acidic conditions as the hydroxide which has a very low solubility product: $K_{sp} = 6.7 \times 10^{-31}$.



The oxides, sulfides and carbonates of most heavy metals possess extremely low aqueous solubility's. Hence, very little of the parent compounds can remain in solution following their formation. Once formed, the soil matrix of the aquifer will then immobilize the precipitates. This process is analogous to technologies used for aboveground metals removal (precipitation/settling/filtration).

This technology's applicability to radionuclides is clear from the geochemistry literature.

Uranium Mechanism

Under ordinary aerobic conditions, uranium exists in the +6 state. In the absence of carbon, the UO_2^{+2} ion is found in acid to slightly basic conditions. Under strongly basic conditions the mixed oxidation state complex U_3O_8 exists. In the presence of carbon, the uranyl ion exists only under clearly acidic conditions. Above a pH of about 5, carbonates prevail. The solid uranyl carbonate exists over a fairly narrow pH range of 5 to 6+ with uranyl carbonate anions existing from near neutral to strongly basic conditions. Throughout this range uranium remains in the +6 oxidation state.

As EARP begins to drop the Eh, the mixed oxide, U_3O_8 , is established over a fairly narrow Eh-pH range. As the process continues and the system begins to go reductive, uranium is reduced to the +4 oxidation state and the solid oxide, UO_2 , is the stable species. In the presence of naturally occurring iron and reduced sulfur, as described earlier, co-precipitation will occur with pyrite (Figure 3). UO_2 is the naturally occurring mineral uraninite. This is the pure uranium mineral found in pitchblende. As such, it can be expected to remain stable.

When Si is a significant species, either with or without carbon, the Eh-pH diagram is significantly changed. However, there is an immobile mineral form, coffinite (USiO_4), that

has a large stability field under reducing conditions, and neutral to acidic conditions, suggesting that EARP can be effective in treating U in the presence of Si as well.

Technetium-99 (⁹⁹Tc) Mechanism

The isotope ⁹⁹Tc is a product of nuclear fission reactions. ⁹⁹Tc has a half-life of 2.13×10^5 years. Reference to the Eh-pH diagram for the system Tc-S-O-H shows that the anion TcO_4^- is the stable species under ordinary aerobic conditions. As EARP technology is implemented and the system moves towards anaerobic, reductive conditions, this ion is reduced first to TcO_2 and then to the mixed oxidation state oxide, Tc_3O_4 . Finally, as reductive conditions stabilize and sulfides are generated, the stable compound TcS_2 becomes the dominant species. Solubility product constants for these several species do not appear to be available, but TcS_2 is known to be stable in the presence of sulfide.²⁰ In the absence of sulfide, Tc_3O_4 is reduced to the hydroxide, $\text{Tc}(\text{OH})_2$. This analysis suggests that EARP should be highly effective for Tc.

An important feature of the *in situ* metals precipitation technology is its irreversibility. Over the natural pH range encountered in the groundwater system at the most contaminated sites, these heavy precipitates have extremely low thermodynamic and kinetic solubilities. This results in a very low probability that the precipitates, once formed, will re-dissolve into the groundwater under natural conditions. Only under extreme changes to the pH or redox conditions in the groundwater could the precipitate resolubilize to any significant extent. These conditions would generally include either very low (less than 4) or very high (greater than 10) pH, or a strongly oxidizing environment (such as that caused by the continuous injection of oxidizing chemicals such as hydrogen peroxide or ozone). These conditions would not be present under any natural scenario.

The geochemistry of the specific heavy metals and radionuclides of primary interest to DOE has recently been reviewed in depth by ARCADIS. The result of this review suggests that this approach will be successful in treating Uranium and Technetium-99 under many conditions commonly found *in situ* and may well treat Strontium as well.

Accomplishments

The potential of this technology for radionuclide applications has been demonstrated recently by a six-month field pilot test that has been electronically published by EPA as a RCRA Cleanup Reform Success story. In this project a 60% reduction of dissolved Uranium and an 83% reduction in TCE was demonstrated.²¹ Scale-up to full scale is underway at this site.

This technology has now been applied at more than 70 commercial and DoD sites. Eighteen of these sites have proceeded to full-scale implementation, while the majority of the rest are either sites with a field pilot test ongoing or where a pilot test has been completed and a full scale system is being designed.

Since numerous case histories for these applications have been presented elsewhere those details will not be repeated here. However 90% or better contaminant removals and multi-million dollar cost savings have been achieved.^{2,3,4,5,7,10,11,12}

Benefits

The primary advantages for the IRZ process include the following:

- *In situ* processes eliminates the need for transferring contaminant mass to other media (such as groundwater pumping and subsequent treatment with air stripping)
- No waste is generated
- Uses innocuous, off-the-shelf, low cost electron donor sources
- Biologically mediated reactions are driven by indigenous microflora without the need for costly and controversial introduced organisms
- The technology is flexible in its engineering application yielding a spectrum of contaminant mass treatment options from passive/containment barrier applications to aggressive source area applications
- promotes reduction of residual contaminant mass through desorption and disruption of the contaminant phase equilibrium
- enhances natural attenuation processes
- Applicable to various geological settings and aquifer conditions
- Electron donor source is highly soluble and can move through both diffusive and advective processes into difficult lithologies such as fractured bedrock
- Can be designed with flexible operation approaches from automated systems to manual bulk application
- Increased rates of mass removal coupled with simple operation requirements reduce long term operations and maintenance costs
- Can be used in tandem with current remediation systems to optimize performance
- Can be designed with minimal site and facility operation disturbance

We plan to continue to apply this technology for a wide range of commercial and governmental clients worldwide (it has already been applied in Europe). We expect these applications to allow us to continue to extend the range of contaminants and conditions under which this technology can be applied. We are beginning a DoE NETL funded demonstration project that will help demonstrate the technology to DoE and provide greater insight into the mechanism and range of applications for radionuclides. A protocol document covering the application of this technology to CAHs will be prepared under ESTCP/AFCEE sponsorship in 2002.

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